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Determination of methylmercury and inorganic mercury in water samples by slurry sampling cold vapor atomic absorption spectrometry in a flow injection system after preconcentration on silica C₁₈ modified

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Abstract

A novel method for preconcentration of methylmercury and inorganic mercury from water samples was developed involving the determination of ng l⁻¹ levels of analytes retained on the silica C₁₈ solid sorbent, previous complexation with ammonium pyrrolidine dithiocarbamate (APDC), by slurry sampling cold vapor atomic absorption spectrometry (SS-CVAAS) in a flow injection (FI) system. Several variables were optimized affecting either the retention of both mercury species, such as APDC concentration, silica C₁₈ amount, agitation times, or their determination, including hydrochloric acid concentration in the suspension medium, peristaltic pump speed and argon flow-rate. A Plackett–Burman saturated factorial design permitted to differentiate the influential parameters on the preconcentration efficiency, which were after optimized by the sequential simplex method. The contact time between mercury containing solution and APDC, required to reach an efficient sorption, was decreased from 26 to 3 min by the use of sonication stirring instead of magnetic stirring. The use of 1 mol dm⁻³ hydrochloric acid suspension medium and 0.75% (m/v) sodium borohydride reducing agent permitted the selective determination of methylmercury. The combination of 5 mol dm⁻³ hydrochloric acid and 10⁻⁴% (m/v) sodium borohydride was used for the selective determination of inorganic mercury. The detection limits achieved for methylmercury and inorganic mercury determination under optimum conditions were 0.96 and 0.25 ng l⁻¹, respectively. The reliability of the proposed method for the determination of both mercury species in waters was checked by the analysis of samples spiked with known concentrations of methylmercury and inorganic mercury; quantitative recoveries were obtained.

Keywords: Preconcentration; Mercury speciation; Water samples; Flow injection; Slurry sampling cold vapor atomic absorption spectrometry

1. Introduction

Mercury species, usually present in natural water samples, are inorganic mercury and methylmercury. Mercury speciation in these samples is of great environmental importance nowadays due to the high toxicity of mercury compounds and their low concentrations, especially when methylmercury is present. Cold vapor (CV) atomic absorption spectrometry (AAS) is one of the most attractive techniques for total mercury determination in environmental and biological samples due to its high sensitivity and reliability [1]. However, this determination at trace amounts requires a prelimi-

nary preconcentration step in order to achieve quantifiable levels.

Although different approaches have been proposed for mercury determinations at trace levels by CVAAS, the recent developments in the field of the preconcentration of mercury compounds from several samples are focused to on-line solid-phase extraction (SPE) in flow injection (FI) systems by the use of a minicolumn. A diversity of combinations between solid sorbent and complexing agent have been employed for preconcentration of both inorganic mercury and methylmercury: (i) on-line formation of mercury diethyldithiocarbamates on silica C₁₈ and quantitative elution of the retained chelates with ethanol [2,3]; (ii) chelation with dithiophosphoric acid diacyl ester (DDTP), adsorption of the corresponding chelates on a C₁₈ column and elution with ethanol [4]; (iii) sorption of the mercury complexes formed with ammonium pyrrolidine

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dithiocarbamate (APDC) on silica C₁₈, which were after eluted with a methanol–acetonitrile–water mixture [5].

Several complexing solid sorbents have been applied to on-line preconcentration of mercury species from natural water samples using different detection techniques [2,3,6,7]. Thus, sulphhydryl cotton permitted to retain methylmercury, ethylmercury and inorganic mercury, which were then eluted with 3 mol dm⁻³ hydrochloric acid [6,7]. Emteborg et al. [8] incorporated a micro-column of dithiocarbamate resin in a FI system to preconcentrate mercury species, being used acidic thiourea as eluent. On the other hand, mercury compounds were preconcentrated on a column containing 2-mercaptobenzimidazol loaded on silica gel and then quantitatively eluted with 0.05 mol dm⁻³ potassium cyanide or 2 mol dm⁻³ hydrochloric acid for inorganic mercury or methylmercury, respectively [9].

Several authors have also proposed off-line enrichment of mercury species on complexing resins. Emteborg et al. [10–12] introduced in natural water samples the complexing resin, prepared by immobilization of dithiocarbamate functional groups on macroporous hydroxyethylmethacrylate spheres, and the suspension was stirred, whereafter the samples were filtered. Mercury species were extracted with acidified thiourea. Determination of inorganic mercury and organomercury compounds was also carried out after preconcentration on dithizone-anchored poly(ethylene glycol dimethacrylate–hydroxyethylmethacrylate) microbeads, when the desorption medium was a mixture of copper sulphate and acidic potassium bromide for organomercury species or dilute nitric acid for inorganic mercury [13]. However, the possibility of direct determination of mercury compounds adsorbed on solid sorbent by slurry sampling (SS) has been investigated. One of the most important advantages of the SS technique is the elimination of the desorption step. So, total mercury was determined in natural gas liquid and condensate using activated carbon by electrothermal (ET)AAS [14]. Phenylmercury was selectively preconcentrated from water samples by living *Escherichia coli* and the amount of organomercury specie retained was determined directly in the biomass slurry by CVAAS [15].

Inorganic mercury and total mercury were quantitatively extracted and, afterwards, determined in biological and environmental solid samples by FI-CVAAS using 10⁻⁴ and 0.75% (m/v) sodium borohydride reducing agent, respectively [16]. Then, this methodology was successfully applied to mercury speciation analysis in fish tissue samples by slurry sampling technique [17]. In the last work, methylmercury was selectively determined when solid samples were suspended in a selective extraction medium for this mercury specie, such as 1 mol dm⁻³ hydrochloric acid, and sodium borohydride concentration was equal to or less than 0.1% (m/v) due to its inability to reduce mercury occluded into the solid particles. Selective determination of inorganic mercury required the suspension of the solid samples in hydrochloric acid concentrations higher than 4 mol dm⁻³ and the use of reducing agent concentrations equal to or less than 0.05% (m/v) because of its inability to reduce methylmercury.

The low concentrations of the most commonly found mercury species in environmental waters (methylmercury and inorganic mercury) led to investigate the possible determination of both

mercury species by slurry sampling technique in a FI-CVAAS system after preconcentration on a solid sorbent. In this sense, the present work combines the advantages of enrichment and the slurry sampling techniques for mercury speciation at ng l⁻¹ concentrations. The introduction of slurried sorbents into FI systems has not been previously reported for mercury speciation analysis by cold vapor generation technique. In this work, silica C₁₈ and APDC were the solid sorbent and complexing agent, respectively. The reaction of mercury species with complexing agents is highly dependent on the sample pH. Nevertheless, previous studies tested little effect of pH values varying from 3 to 9 on mercury recovery. The preconcentration parameters were after optimized by the sequential simplex method. Furthermore, the advantages of the use of ultrasonic energy during sorption step were investigated in order to facilitate the solid-phase extraction process and to reduce the time involved. Following sorption, the solid sorbent was suspended in hydrochloric acid concentrations ranging from 1 to 5 mol dm⁻³, containing Triton X-100 as dispersing agent. Although the differentiation between total mercury and inorganic mercury was based on sodium borohydride reducing agent concentration (10⁻⁴ and 0.75% (m/v) for inorganic mercury and total mercury determinations, respectively), the possibility of separate determination of methylmercury and inorganic mercury was also studied. The proposed methodology was applied to the analysis of spiked water samples.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer flow injection mercury system (FIMS) Model 400 (Überlingen, Germany), equipped with a flow injection analysis system (FIAS) and an autosampler Model AS-91, was used for all mercury determinations. This system consisted of two peristaltic pumps (P₁ and P₂), a flow-meter, a cylindrical gas–liquid separator partially filled with glass beads, a six-way injection valve equipped with a sample loop and a quartz cell (25 cm length with quartz windows). The slurry was injected into the system during certain time, while it was being stirred, and transported in an acid carrier to the chemifold where it was mixed with the sodium borohydride reducing agent along a reduction coil of 5.0 cm (R₁). Then, mercury vapor was purged from the liquid-phase along a stripping coil of 15 cm (R₂) with an argon stream of 40 ml min⁻¹, before its entrance into the gas–liquid separator and then swept into the quartz cell.

The peristaltic pumps, injection time and data acquisition were controlled through Perkin-Elmer AAWinLab Atomic absorption spectroscopy software (Norwalk, CT, USA). The FIAS program used for all mercury determinations is shown in Table 1. The sample loop (500 µl) was filled by means of pump P₂. The acid carrier, reducing agent and waste solution from the gas–liquid separator were pumped using peristaltic pump P₂ through Tygon tubes and the waste solution from the injection valve was pumped with a peristaltic pump P₁ also through a Tygon tube. The flow injection manifold is shown in Fig. 1. Acid carrier flow-rates were 5.5 and 9.5 ml min⁻¹ for inorganic mercury and total mercury determination, respectively.

Table 1
FIAS 400 program for mercury determination

Step	Time (s)	P ₁ speed (rpm)	P ₂ speed (rpm)	Valve position	Read
Prefill	15	100	120	Fill	No
1	10	100	120	Fill	No
2	15	0	120	Inject	Yes
3	0	–	–	Fill	No

Reducing agent flow-rates were 4.0 and 6.5 ml min⁻¹ for inorganic mercury and total mercury determination, respectively. The manifold tubing was made of 1.0 mm i.d. Teflon (FEP). An integration time of 20 s and peak height measurement mode were used.

A Fisher Scientific magnetic stirrer (Fair Lawn, NJ, USA), a Sonics and Materials sonication probe Model VC50S (Danbury, CT, USA) with 20 kHz and 50 W, a Fisher Scientific centrifuge and a Fisher Scientific pHmeter Model 915 were used for enrichment purposes. MultiSimplex KB software (Karls Krona, Sweden) was used for the optimization of preconcentration method.

2.2. Reagents, standards and samples

All solutions were prepared in deionized water produced by a Barnstead E-Pure system and the chemicals used were of analytical-reagent grade. The 10⁻⁴ and 0.75% (m/v) solutions of sodium borohydride reducing agent for inorganic mercury and total mercury determination was prepared daily by dissolution of the appropriate amount of the solid reagent (Alfa Aesar, Ward Hill, MA, USA) in a 0.001 and 1.0% (m/v) sodium hydroxide solution, respectively. The carrier was 3.0% (v/v) hydrochloric acid. The stock standard solution of mercury nitrate (1000 mg l⁻¹), was supplied by Alfa Aesar. The stock standard solution of methylmercury chloride (100 mg l⁻¹), was prepared by dissolving the appropriate amount of the solid reagent from Strem Chemicals (Newburyport, MA, USA) in a minimum volume of methanol and diluting it to volume with deionized water. The working standard solutions for each individual mercury species were prepared daily by appropriately diluting the

10 mg l⁻¹ (as Hg) standard solutions, prepared weekly, with dilute hydrochloric acid. All standards were stored at 4 °C away from light before use.

Drinking and pond water samples were filtered through 0.45 µm membranes from Millipore (Bedford, MA, USA).

2.3. Preconcentration procedure

A sample volume of 90 ml was introduced in a polyethylene centrifuge tube. Then, pH was adjusted to values comprised between 3 and 9, and the appropriate amount of APDC was added in order to achieve a concentration of 0.0041 mol dm⁻³. The mixture was magnetically stirred during 26 min or sonicated during 3 min at 50% power in order to improve the complexes formation. Then, 37.4 mg of silica C₁₈ were suspended and the resulting suspension was magnetically stirred for 30 min to achieve an efficient retention of mercury species on solid sorbent. The solid particles were separated by centrifugation during 5 min at 5000 rpm. Then, they were slurried in 10 ml of 1 or 5 mol dm⁻³ hydrochloric acid (containing 0.02% (v/v) Triton X-100 as dispersing agent) for methylmercury determination or inorganic and total mercury determination, respectively. The slurries were magnetically stirred for 10 min to obtain a homogeneous dispersion and maintained under magnetic stirring during the injection into the FI system. Blanks were prepared with the same reagents undergoing a similar treatment.

2.4. Plackett–Burman design

The Plackett–Burman fractional factorial design was used to estimate the influence of some variables on preconcentration efficiency of mercury species. The concentration used of methylmercury and inorganic mercury was 0.5 µg l⁻¹. A design for seven factors (Table 2) was selected using as many columns as variables studied. Therefore, only eight experiments were carried out by three replicates. The variables investigated with their factor designators and the lower (–) and upper (+) levels for each one of them are shown in Table 3. The response was concentration recovered of inorganic mercury and total mercury using 10⁻⁴ and 0.75% (m/v) sodium borohydride reducing agent, respectively. A variable was considered as significant when the difference between the mean value of the results obtained for upper and lower levels was higher than the double of the mean standard deviation.

Table 2
Plackett–Burman design

Experiment	A	B	C	D	E	F	G
1	+	+	+	–	+	–	–
2	+	+	–	+	–	–	+
3	+	–	+	–	–	+	+
4	–	+	–	–	+	+	+
5	+	–	–	+	+	+	–
6	–	–	+	+	+	–	+
7	–	+	+	+	–	+	–
8	–	–	–	–	–	–	–

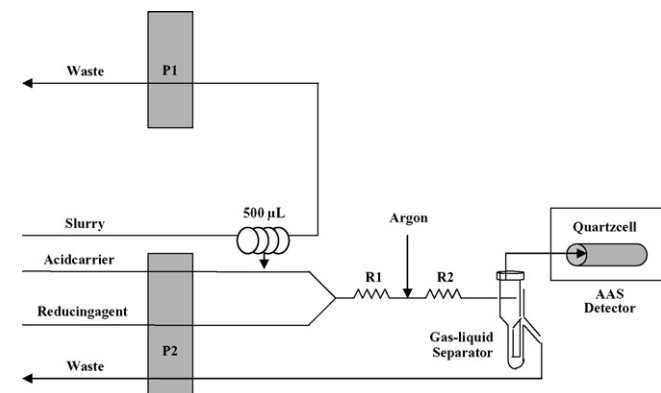


Fig. 1. Flow injection manifold used for mercury determinations. P₁ and P₂ are peristaltic pumps; R₁ and R₂ are reaction coils.

2.5. Sequential simplex method

Only the significant variables were after optimized by using the sequential simplex method. The optimal experimental conditions were: maximum recovery for methylmercury and inorganic mercury using 5 mol dm⁻³ hydrochloric acid, maximum recovery for methylmercury when 1 mol dm⁻³ hydrochloric acid was used and minimum recovery for inorganic mercury using 1 mol dm⁻³ hydrochloric acid. The response variables evaluated were the concentration recovered of methylmercury and inorganic mercury for a 0.5 µg l⁻¹ standard aqueous solution. The experiments were performed in three replicates.

3. Results and discussion

3.1. Factor screening

The main effect of the different factors for inorganic mercury and total mercury determination by SS in a FI-CVAAS system after preconcentration on silica C₁₈ modified with APDC complexing agent was checked using a Plackett–Burman saturated factorial design. As shown in Table 3, the first four factors were related to the enrichment procedure, the other three to determination of mercury retained. So, it was possible to detect the most significant variables by performing few experiments (*k* factors were studied in *k* + 1 runs). The results obtained are shown in Fig. 2, which indicated: agitation time with APDC, silica C₁₈ amount, agitation time with silica C₁₈, P₂ speed and argon flow-rate were significant variables for methylmercury determination as total mercury (using 0.75% (m/v) sodium borohydride reducing agent; see Fig. 2a); APDC concentration, hydrochloric acid concentration and argon flow-rate gave significant effects for inorganic mercury determination as total mercury (using 0.75% (m/v) sodium borohydride reducing agent; see Fig. 2b); and silica C₁₈ amount, hydrochloric acid concentration and P₂ speed were significant variables for inorganic mercury determination (using 10⁻⁴% (m/v) sodium borohydride reducing agent; see Fig. 2c). However, hydrochloric acid concentration, P₂ speed and argon flow-rate were fixed at 1 or 5 mol dm⁻³ for methylmercury or inorganic mercury determination, 120 rpm and 40 ml min⁻¹, respectively, due to the similar influence observed in all figures: positive for hydrochloric acid concentration in inorganic mercury determination and P₂ speed;

Table 3
Variables studied for mercury species preconcentration

Variable	Factor	Lower level (–)	Upper level (+)
APDC concentration (mol dm ⁻³)	A	0.001	0.005
Agitation time with APDC (min)	B	0	30
Silica C ₁₈ amount (mg)	C	10	50
Agitation time with silica C ₁₈ (min)	D	1	30
Hydrochloric acid concentration (mol dm ⁻³)	E	1	5
P ₂ speed (rpm)	F	75	120
Argon flow-rate (ml min ⁻¹)	G	40	75

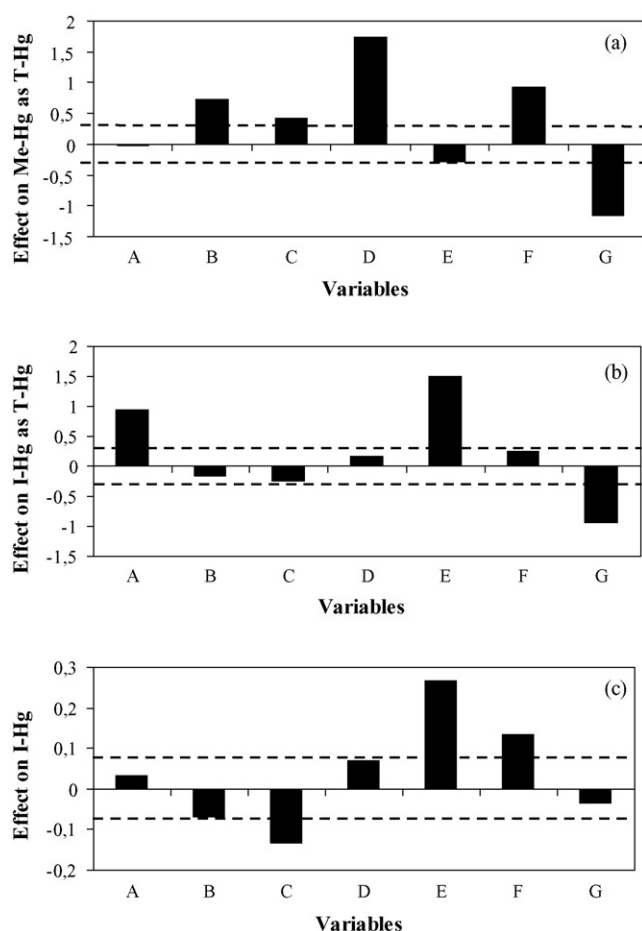


Fig. 2. Effect of the different variables in the determination of methylmercury as total mercury (a), inorganic mercury as total mercury (b) and inorganic mercury (c) by SS in a FI-CVAAS system after preconcentration on silica C₁₈ modified with APDC complexing agent, using a Plackett–Burman saturated factorial design. The effect was calculated as the difference between the mean value of the results obtained for upper and lower levels. Dashed lines show double of the mean standard deviation.

or negative for hydrochloric acid concentration in methylmercury determination and argon flow-rate.

3.2. Optimization of the experimental conditions

The sequential simplex method was used to optimize the influential variables that were not previously selected, including APDC concentration, agitation time with APDC, silica C₁₈ amount and agitation time with silica C₁₈. The step size and reference value for each variable are presented in Table 4. The simplex progressed towards the optimum recovery for

Table 4
Step size and reference value of the optimized variables

Variable	Step size	Reference value
APDC concentration (mol dm ⁻³)	0.0020	0.0050
Agitation time with APDC (min)	10	15
Silica C ₁₈ amount (mg)	20.0	20.0
Agitation time with silica C ₁₈ (min)	20	30

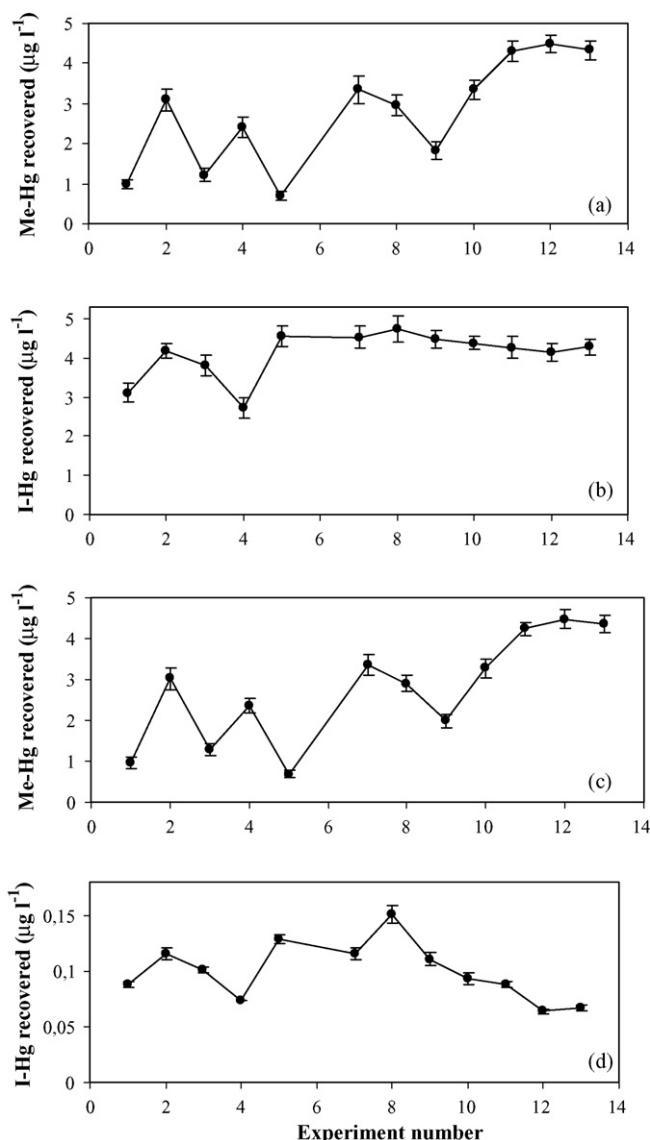


Fig. 3. Evolution of concentration recovered along the sequential simplex method of methylmercury using 5 mol dm^{-3} hydrochloric acid (a), inorganic mercury using 5 mol dm^{-3} hydrochloric acid (b), methylmercury using 1 mol dm^{-3} hydrochloric acid (c) and inorganic mercury using 1 mol dm^{-3} hydrochloric acid (d). Mercury concentration was determined by SS in a FI-CVAAS system involving 0.75% (m/v) sodium borohydride reducing agent, after preconcentration on silica C_{18} modified with APDC complexing agent.

methylmercury and inorganic mercury using 1 and 5 mol dm^{-3} hydrochloric acid. Fig. 3 shows the evolution of the responses along 12 experiments. The experiment 6 was not carried out because the software proposed to avoid silica C_{18} . The simplex stopped when three consecutive experiments led to no significantly different response. The greatest similitude found between the evolution of both variables studied and response values corresponded to: (i) methylmercury recovery and silica C_{18} amount; (ii) inorganic mercury recovery and APDC concentration. Taking into account the response values obtained, the optimized experimental variables were $0.0041 \text{ mol dm}^{-3}$ APDC with a magnetic stirring time of 26 min and 37.4 mg of silica C_{18} with magnetic stirring for 30 min. Methylmercury and inorganic mer-

cury form charged complexes with the chloride ion MeHgCl_2^- and HgCl_4^{2-} , respectively. So, an increase of hydrochloric acid concentration promotes the HgCl_4^{2-} formation. Furthermore, an incomplete desorption of methylmercury using 1 mol dm^{-3} hydrochloric acid should be compensated with a little attack of 0.75% (m/v) sodium borohydride reducing agent on methylmercury retained on the solid particles. Previous studies, developed in our laboratory, revealed that the complexes formed between methylmercury and APDC are more easily reducible (36%) than those corresponding to inorganic mercury.

3.3. Ultrasound-assisted sorption step

Magnetic and sonication stirrings were compared in order to reduce the time involved in the sorption step, including complexation reaction between mercury species and APDC complexing agent and, afterwards, retention on silica C_{18} of the complexes formed. First, the power and time of sonication were optimized for the complexes formation phase. The concentration recovered of inorganic mercury was quantitative for sonication power and sonication time values of 50% and 3 min, respectively. Inorganic mercury recovery increased with sonication time for times less than 3 min and sonication powers comprised between 50 and 75%. However, the use of sonication times higher than 3 min had an opposite effect. On the other hand, this recovery also increased when the sonication power was increased from 30 to 50%, while it decreased when the sonication power was increased from 50 to 75%. Although no significant effect was found for methylmercury when both sonication parameters were modified, the concentration recovered of methylmercury was also quantitative in all experiments. Therefore, sonication power and sonication time values of 50% and 3 min, respectively, were selected for further studies.

The power and time of sonication were also optimized for the effective retention of the complexes on silica C_{18} . Sonication power had an opposite effect for methylmercury and inorganic mercury determinations. While concentration recovered of inorganic mercury decreased when sonication power was increased, concentration recovered of methylmercury increased when sonication power was increased from 30 to 50% and it decreased for power values higher than 50%. Nevertheless, all recoveries investigated were less than 32%. Furthermore, the sonication time had no effect on the recoveries studied. So, magnetic stirring was selected for the performance of this second phase of the sorption step in further experiments.

3.4. Analytical figures of merit

The analytical performance of the proposed off-line preconcentration and slurry sampling methodology in a FI-CVAAS system was evaluated using the optimum experimental conditions. Linear calibration curves were achieved by the treatment of a series of methylmercury and inorganic mercury standards of up to $1.0 \mu\text{g l}^{-1}$, because of the enrichment was not efficient when higher mercury concentrations were used. So, recoveries of 58.9 ± 2.8 , 72.8 ± 2.8 , 55.5 ± 2.4 and $78.9 \pm 4.4\%$ were found for the determination of $2 \mu\text{g l}^{-1}$ methylmercury as total

mercury (using 5 mol dm⁻³ hydrochloric acid and 0.75% (m/v) sodium borohydride reducing agent), inorganic mercury as total mercury (using 5 mol dm⁻³ hydrochloric acid and 0.75% (m/v) sodium borohydride reducing agent), methylmercury (using 1 mol dm⁻³ hydrochloric acid and 0.75% (m/v) sodium borohydride reducing agent) and inorganic mercury (using 5 mol dm⁻³ hydrochloric acid and 10⁻⁴% (m/v) sodium borohydride reducing agent), respectively. The slopes obtained for the calibration lines, expressed as mean value \pm standard deviation ($n=3$), were 0.149 ± 0.006 , 0.146 ± 0.004 , 0.145 ± 0.006 and 0.199 ± 0.010 $\mu\text{g l}^{-1}$ for the determination of methylmercury as total mercury, inorganic mercury as total mercury, methylmercury and inorganic mercury, respectively. The correlation coefficient (r) was always higher than 0.9997. As expected, the slopes of the calibration lines for total mercury determination obtained with methylmercury and inorganic mercury standards were not significantly different (t -test, $P=0.05$). Furthermore, the slope of the calibration line for inorganic mercury determination was greater than that corresponding to total mercury and methylmercury determination. The detection limit based on the amount necessary to yield a net signal equal to three times the standard deviation of the blank was 2.6, 2.6 and 0.48 ng l⁻¹ for total mercury, methylmercury and inorganic mercury, respectively. The best detection limit corresponded to inorganic mercury determination because of the use of a little concentration of sodium borohydride. The precision, expressed as the relative standard deviation ($n=10$) for a 0.50 $\mu\text{g l}^{-1}$ mercury standard was less than 3% for all mercury determinations.

It should be noted that the detection limits obtained by the proposed method are comparable to those reported for other preconcentration approaches of mercury species based on: (i) on-line SPE in FI systems by the use of a minicolumn filled with complexing solid sorbent, with detection limits of 16 ng l⁻¹ [2] or 10 ng l⁻¹ [4] when CVAAS was used as detection technique; and 6 ng l⁻¹ for methylmercury determination [6], or 0.07 and 0.05 ng l⁻¹ for inorganic mercury and methylmercury

determination, respectively [9], when CVAFS was the detection technique employed; (ii) off-line enrichment on complexing resins; (iii) retention on solid sorbent and slurry sampling technique with a detection limit of 2000 ng l⁻¹ for total mercury determination by ETAAS [14], or 50 ng l⁻¹ for phenylmercury determination by CVAAS [15]. As can be seen the lowest detection limits not only corresponded to the use of more sensitive detection techniques, such as CVAFS, but also to the great sample volume required (1 l).

With the aim of decreasing the detection limits, the effect of different sample volumes containing the same amount (45 ng) of both analytes on the recovery of mercury species was investigated. The results obtained offered the use of sample volumes of up to 270 and 180 ml for methylmercury and inorganic mercury determination, respectively, achieving recoveries higher than 92%. Therefore, the detection limits decreased to 0.96 and 0.25 ng l⁻¹ for methylmercury and inorganic mercury determination, respectively.

3.5. Determination of methylmercury, inorganic mercury and total mercury in spiked water samples

The developed method was applied to the analysis of water samples. As the concentration of methylmercury and inorganic mercury was not detectable in these samples, the accuracy of the proposed method for mercury speciation in water samples was checked by the analysis of deionized water in the presence of interfering ions (0.1 mg l⁻¹ of Al³⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe³⁺, Mn²⁺, Ni²⁺, Pb²⁺ and Zn²⁺; 10 mg l⁻¹ of K⁺ and Mg²⁺; 50 mg l⁻¹ of Ca²⁺; 100 mg l⁻¹ of Na⁺; 25 mg l⁻¹ of Cl⁻ and SO₄²⁻; and, finally, 300 mg l⁻¹ of HCO₃⁻), drinking water and pond water samples; all of them spiked with different concentrations of methylmercury and inorganic mercury (30–90 ng l⁻¹). The results obtained can be seen in Table 5, showing that the recovery values were greater than 95% for methylmercury, inorganic mercury and total mercury determinations. The relative

Table 5
Determination of methylmercury, inorganic mercury and total mercury in spiked water samples

Mercury added (ng l ⁻¹)	Me-Hg recovered (ng l ⁻¹) ^a	I-Hg recovered (ng l ⁻¹) ^a	T-Hg recovered (ng l ⁻¹) ^a
Deionized water containing interfering ions			
0	<LOD	<LOD	<LOD
30 (Hg ²⁺) + 30 (MeHg ⁺)	30 \pm 3	29 \pm 2	62 \pm 4
60 (Hg ²⁺) + 60 (MeHg ⁺)	58 \pm 4	59 \pm 2	115 \pm 7
90 (Hg ²⁺) + 90 (MeHg ⁺)	87 \pm 4	86 \pm 4	176 \pm 8
Drinking water			
0	<LOD	<LOD	<LOD
30 (Hg ²⁺) + 30 (MeHg ⁺)	30 \pm 3	30 \pm 2	60 \pm 5
60 (Hg ²⁺) + 60 (MeHg ⁺)	58 \pm 5	58 \pm 3	119 \pm 9
90 (Hg ²⁺) + 90 (MeHg ⁺)	87 \pm 5	87 \pm 5	173 \pm 12
Pond water			
0	<LOD	<LOD	<LOD
30 (Hg ²⁺) + 30 (MeHg ⁺)	29 \pm 3	30 \pm 2	59 \pm 6
60 (Hg ²⁺) + 60 (MeHg ⁺)	58 \pm 4	58 \pm 3	116 \pm 8
90 (Hg ²⁺) + 90 (MeHg ⁺)	86 \pm 6	87 \pm 5	172 \pm 10

^a Mean value \pm standard deviation ($n=3$).

standard deviations for three replicate samples submitted to the same spiking, treatment and detection procedures were less than 10%. Therefore, both the accuracy and precision were satisfactory.

4. Conclusions

The direct introduction of slurried solid sorbent into a FI system for mercury speciation analysis by CV generation technique combined with AAS has successfully permitted the determination of ng l^{-1} levels of methylmercury and inorganic mercury in water samples, previously complexed with APDC and retained on silica C_{18} . All variables involved in the steps of mercury preconcentration and slurry analysis were optimized by the sequential simplex method, which provided a viable option for this purpose when the experimental parameters to optimize were previously chosen by a Plackett–Burman saturated factorial design. On the other hand, sonication stirring resulted to be a valuable alternative to magnetic stirring for achieving efficient complexation between mercury species and APDC in much less time. Thus, the time-consuming step was sorption of the complexes on the silica C_{18} sorbent. The detection limits obtained for methylmercury and inorganic mercury were comparable to the majority of the previously reported, including those related to other more sensitive detection techniques, such as CVAFS. The main advantage of this method is its inexpensive instrumentation along with a relatively good sensitivity and precision. The applicability of the proposed methodology to the determination of both mercury species in water samples was demonstrated.

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References

- [1] B. Welz, M. Sperling, Atomic Absorption Spectrometry, 3rd ed., Wiley, Weinheim, 1999.
- [2] M. Fernández García, R. Pereiro García, N. Bodel García, A. Sanz Medel, Talanta 41 (1994) 1833.
- [3] R. Martínez Blanco, M. Tagle Villanueva, J.E. Sánchez Uría, A. Sanz-Medel, Anal. Chim. Acta 419 (2000) 137.
- [4] A.C.P. Monteiro, L.S.N. de Andrade, R.C. de Campos, Fresenius J. Anal. Chem. 371 (2001) 353.
- [5] X. Yin, W. Frech, E. Hoffmann, C. Lüdke, J. Skole, Fresenius J. Anal. Chem. 361 (1998) 761.
- [6] J. Wei, C.W. McLeod, Talanta 39 (1992) 1537.
- [7] M.L. Mena, C.W. McLeod, P. Jones, A. Withers, V. Minganti, R. Capelli, P. Quevauviller, Fresenius J. Anal. Chem. 351 (1995) 456.
- [8] H. Emteborg, D.C. Baxter, W. Frech, Analyst 118 (1993) 1007.
- [9] H. Bagheri, A. Gholami, Talanta 55 (2001) 1141.
- [10] S. Hånström, C. Briche, H. Emteborg, D.C. Baxter, Analyst 121 (1996) 1657.
- [11] H. Emteborg, D.C. Baxter, M. Sharp, W. Frech, Analyst 120 (1995) 69.
- [12] H. Emteborg, H.-W. Sinemus, B. Radziuk, D.C. Baxter, W. Frech, Spectrochim. Acta B 51 (1996) 829.
- [13] B. Salih, R. Say, A. Denizli, O. Genc, E. Piskin, Anal. Chim. Acta 371 (1998) 177.
- [14] J. Shiowatana, A. Siripinyanond, W. Waiyawat, S. Nilmanee, Atom. Spectrosc. 20 (1999) 224.
- [15] L.C. Robles, J.C. Feo, A.J. Aller, Anal. Chim. Acta 423 (2000) 255.
- [16] S. Río Segade, J.F. Tyson, Spectrochim. Acta 58B (2003) 797.
- [17] S. Río Segade, J.F. Tyson, J. Anal. Atom. Spectrom. 18 (2003) 268.